

PROCESS FOR DENITRIFICATION OF EXHAUST GASSES,
PARTICULARLY FOR LEAN OPERATED INTERNAL COMBUSTION ENGINES

[0001] The invention concerns a process for denitrification of primarily lean operated internal combustion engines according to the precharacterizing portion of Patent Claim 1.

[0002] EP 0 890 389 A1 discloses an NOx storage catalytic converter for cleansing the exhaust gasses of vehicle exhaust gas systems. The disclosed storage catalytic converter is comprised of two material components, wherein the one material component serves for intermediate storage of nitrogen oxide during lean operation of the vehicle internal combustion engine and the other material component is a catalytic material with three-way characteristics in which, during short term rich exhaust gas operation, stored nitrogen oxide is released and converted to molecular nitrogen (N₂).

[0003] The required relationship between the lean operating phase and the rich operating phase in the combustion control of the vehicle internal combustion engine is determined by various parameters such as the NOx storage capacity of the material, the amount of NOx arriving, the exhaust gas temperature and, in the case of sulfur-containing exhaust gas, by the sulfur content. In order to achieve a low fuel consumption, it is desired to operate the vehicle internal combustion engine as long as possible with lean operating phases and as briefly as possible with rich operating phases. The NOx storage catalytic converter thus operates discontinuously, since the combustion control of the exhaust gas must be switched alternately from lean to rich.

[0004] EP 0 707 882 A1 discloses an NOx storage catalytic converter with an aluminum oxide containing carrier, upon which a

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Ti-Zr mixed oxide is applied. On the aluminum oxide containing carrier material there is further provided, for the collection and storage of nitrogen oxide, a compound selected from the group of elements of the alkali metals, alkali earth metals and rare earth. The aluminum oxide containing carrier material is further doped with a noble metal, for example palladium (Pd), platinum (Pt) or rhodium (Rh).

[0005] Alternative published embodiments of the known NOx storage catalytic converter exhibit a carrier material of a mixed oxide of the elements titanium (Ti), zircon (Zi) and yttrium (Y). The employed alkali metals, alkali earth metals or rare earth for storage of nitrogen oxide have the disadvantages of a low temperature stability as well as a low SO₂-tolerance.

[0006] EP 0 927 571 A2 discloses a further NOx storage catalytic converter which is free of alkali metals, alkali earth metals and rare earth, with a carrier material comprising at least 50 wt.% aluminum oxide, which is doped with platinum and optionally with palladium, rhodium or other compounds. The disclosed aluminum oxide containing NOx storage catalyst (Pt/Al₂O₃ catalytic converter) absorbs nitrogen oxide from the exhaust gas in the lean motor operating phase and releases the nitrogen oxide during the rich motor operating phase with simultaneous conversion on platinum.

[0007] In the disclosed NOx storage catalytic converter the relationship of the lean motor operating phase to the rich motor operating phase was found to be problematic. It is only in a lean-rich cycle with respectively equal durations of a lean and rich motor operating phases (for example 60 seconds each) that, at a temperature of 350°C, a maximum NOx conversion of approximately 65% could be achieved. With shorter duration of

the rich motor operating phase in comparison to the lean motor operating phase, a lower NOx conversion is achieved.

[0008] It is the task of the invention to provide a process for denitrification of exhaust gasses from primarily lean operated internal combustion engines, which process achieves a good effectiveness even in the case of very short rich motor operating phases.

[0009] The solution to the task is set forth in Patent Claim 1. Further advantageous embodiments of the inventive process are set forth in the further claims.

[00010] In the inventive process the porous carrier substance is comprised of at least 50 wt.% zirconium oxide, titanium oxide, silicon oxide or a zeolite, or a mixture of two or more of these compounds.

[00011] The BET-surface of the above-listed carrier substances is preferably between 10 and 500 m²/g. The rhodium concentration upon the listed carrier materials is preferably 0.1 to 2 wt.%, but can however be appropriately increased or reduced for targeted changes of the solids characteristics.

[00012] For improvement of the nitrogen oxide storage and catalytic characteristics of the process it is possible to supplementally apply one or more noble metals, for example platinum, iridium or palladium upon the porous carrier substance. Thereby the activity of the material may be significantly increased.

[00013] In an advantageous embodiment of the inventive process the nitrogen oxide storing and catalytically effective solid can, commensurate with the intended use, be employed in various forms

such as, for example, pellets or extrudates. The solid employed in the inventive process can however also be applied upon a geometric or shaped carrier made, for example, of metal or ceramic.

[00014] The two noble metals applied upon the porous carrier substance (rhodium + supplemental noble metal) can be used together in accordance with the invention in the following manner:

Micro-Mixture

Both noble metals are provided as atomic mixtures upon the same porous carrier substance, which for its part is applied upon a geometric carrier.

Macro-Mixture

Both noble metal components are individually provided on respective separate porous carrier materials, wherein the carrier materials could be the same or different type. The respective noble metal doped carrier substances are applied as a powder mixture onto a geometric carrier.

Layer Arrangement

Noble metal components are provided, separately, in layers upon the porous carrier substances, which porous carrier substances are then provided upon a geometric carrier.

Structured Arrangement

Both noble metal components are provided respectively individually upon porous carrier substances, which are respectively, separately from each other, applied upon different geometric carriers, for example in serial arrangement.

[00015] The inventive process is particularly suitable for employment in internal combustion vehicle motors, and in particular diesel motors, stoichiometrically and lean operated Otto motors, as well as gas motors.

[00016] The invention will be described in greater detail below on the basis of the experimental results with reference to the figures. There is shown:

Fig. 1 the temperature-dependent NOx conversion of an inventive Pt/Rh/ZrO₂-solid in λ -alternating operation,

Fig. 2 the NOx concentration over time using the inventive Pt/Rh/ZrO₂-solid at T=280°C in λ -alternating operation.

[00017] During the experiments a lean operating phase of 90 seconds was alternated with a rich operating phase of 4 seconds. The reaction-gas had the following compositions in the lean and rich operating conditions:

	Lean ($\lambda=2.4$)	Rich ($\lambda=0.7$)
NO	280 Vol.-ppm	280 Vol.-ppm
O ₂	12.5 Vol.-%	0 Vol.-%
CO	0.25 Vol.-%	9.3 Vol.-%
H ₂	1500 Vol.-ppm	2.6 Vol.-%
Propene	75 Vol.-ppm	2700 Vol.-ppm
CO ₂	10 Vol.-%	10 Vol.-%
H ₂ O	10 Vol.-%	10 Vol.-%
N ₂	Rest	Rest

[00018] The space velocity in the operating phases corresponded to 20000 1/h.

[00019] Fig. 1 shows NOx conversion of the reaction gas for a catalytic converter operated in λ -alternating operation, using an exemplary Pt/Rh/ZrO₂ catalytic converter with 1.5 wt.% Pt and 0.5 wt.% Rh on microporous zinc oxide, as a function of the temperature (measured in advance of the catalytic converter). The catalytic converter was operated alternately 90 seconds lean and 4 seconds rich using synthetic exhaust gas. Simultaneously thereto a temperature program from 100°C to 500°C was carried out with a temperature ramp of 2°C/min. From the difference between the amount of nitrogen oxide supplied to the catalytic converter and the amount exiting from the catalytic converter, it was possible to determine an integral NOx conversion per lean-rich cycle carried out.

[00020] With the present catalytic converter an NOx conversion maximum was observed in the temperature range between 160°C and 500°C. This maximum was plotted at a temperature of approximately 280°C and represented approximately 90%. Further, the present Pt/Rh/ZrO₂ catalytic converter achieved an NOx conversion of at least 50% over a broad temperature range (160°C-370°C).

[00021] In Fig. 2 there is shown for the Pt/Rh/ZrO₂ catalytic converter described in Fig. 1, operated for exemplary purposes at T=280°C - the temperature of the greatest NOx conversion - a plot over time of the NOx concentration downstream of the NOx storage material, measured in the λ -cycle operation of the reaction gas. The NOx input concentration in this experiment corresponded to 280 ppm. In Fig. 2 on the left ordinate the NOx concentration is

shown in ppm, and on the right ordinate the λ -signal is shown. The upper curve shows the course of the λ -signal, the lower curve the corresponding time sequence of the NOx concentration. From this, according to the shown λ -signal prior to the NOx storage material, the lean operating phases ($\lambda=2.4$) and the rich operating phases ($\lambda=0.7$) can be designated.

[00022] During the lean operation phase nitrogen oxide storage is determined wherein, on the basis of increasing loading of the nitrogen oxide storing solid, the NOx concentration downstream of the catalytic converter slowly increases. Therein the NOx concentration at the beginning of a lean operating phase (time point at which in the λ -cycle operating λ achieves the value 2.4), for example at approximately time 113.3 min., is approximately 10 ppm and increases towards the end of the lean operating phase after 90 seconds, corresponding to approximately time 114.8 min., up to approximately 80 ppm. The subsequent rich operating phase of approximately 4 s leads to a short time NOx concentration peak with a maximum at approximately 200 ppm, which lies clearly below the NOx intake concentration.

[00023] Accordingly the nitrogen oxide bonded to the NOx storage material is released. A renewed alternation back to lean operation leads then to a lowering of the NOx concentration to approximately 10 ppm, and the cycle of the NOx storage and NOx release is repeated. Thereby an integral nitrogen oxide conversion of approximately 90% per cycle is achieved with the Pt/Rh/ZrO₂ catalytic converter.